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Nitrous oxide water column distribution during the transition from anoxic to oxic conditions in the Baltic Sea

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Abstract

In January 2003, a major inflow of cold and oxygen-rich North Sea Water in the Baltic Sea terminated an ongoing stagnation period in parts of the central Baltic Sea. In order to investigate the role of North Sea Water inflow to the Baltic Sea with regard to the production of nitrous oxide (N_2O), we measured dissolved and atmospheric N_2O at 26 stations in the southern and central Baltic Sea in October 2003.

At the time of our cruise, water renewal had proceeded to the eastern Gotland Basin, whereas the western Gotland Basin was still unaffected by the inflow. The deep water renewal was detectable in the distributions of temperature, salinity, and oxygen concentrations as well as in the distribution of the N_2O concentrations: Shallow stations in the Kiel Bight and Pomeranian Bight were well-ventilated with uniform N_2O concentrations near equilibrium throughout the water column. In contrast, stations in the deep basins, such as the Bornholm and the Gotland Deep, showed a clear stratification with deep water affected by North Sea Water. Inflowing North Sea Water led to changed environmental conditions, especially enhanced oxygen (O_2) or declining hydrogen sulfide (H_2S) concentrations, thus, affecting the conditions for the production of N_2O. Pattern of N_2O profiles and correlations with parameters like oxygen and nitrate differed between the basins. The dominant production pathway seems to be nitrification rather than denitrification.

No indications for advection of N_2O by North Sea Water were found. A rough budget revealed a significant surplus of in situ produced N_2O after the inflow. However, due to the permanent halocline, it can be assumed that the formed N_2O does not reach the atmosphere. Hydrographic aspects therefore are decisive factors determining the final release of produced N_2O to the atmosphere.

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1 Introduction

1.1 Nitrous oxide

Nitrous oxide (N_2O) is an important atmospheric trace gas which influences, directly and indirectly, the Earth's climate: In the troposphere, it acts as a greenhouse gas with a relatively long atmospheric lifetime of 114 years (Prather et al., 2001). In the stratosphere it is the major source for nitric oxide radicals, which are involved in one of the main ozone reaction cycles (WMO, 2003).

N_2O is mainly formed during microbial processes such as nitrification and denitrification. Nitrification is an aerobic two-step process in which ammonium is oxidized to nitrate. In this process, in which typically two groups of bacteria are involved, N_2O is assumed to be a by-product, the exact metabolism however is still under discussion (Ostrom et al., 2000). In suboxic habitats, nitrate can be reduced by denitrification to molecular nitrogen, with N_2O as an intermediate (Cohen and Gordon, 1978). N_2O may also be produced by coupled nitrification and denitrification at oxic/suboxic boundaries, due to the transfer of intermediates such as nitrate and nitrite (Yoshinari et al., 1997). Other possibilities are the production of N_2O during nitrifier-denitrification or aerobic denitrification (Wrage et al., 2001). Both processes enable nitrifiers to oxidize NH_4^+ to NO_2^-, followed by the reduction of NO_2^- to N_2O or N_2 (Robertson and Kuenen, 1984; Robertson et al., 1988; Richardson, 2000). In anoxic habitats N_2O is used, instead of oxygen, as an electron acceptor (Elkins et al., 1978; Cohen and Gordon, 1978).

The yield of N_2O during these processes strongly depends on the concentration of dissolved oxygen and nitrate (Brettar and Rheinheimer, 1991; Goreau et al., 1980; Vollack and Zumft, 2001; Wetzel, 1983), with maximal N_2O accumulation at the interface between oxic and suboxic layers and depletion in anoxic layers (Codispoti et al., 2005). Positive correlations between N_2O and oxygen or nitrate are commonly interpreted as an indication of N_2O production by nitrification (Yoshinari, 1976; Yoshida et al., 1989; Cohen and Gordon, 1978). In contrast, production by denitrification is inferred by missing correlations (Elkins et al., 1978; Cohen and Gordon, 1978). However, up to now

the dominant production pathway for N_2O on the global scale remains unclear and is discussed controversially (Codispoti et al., 2001; Popp et al., 2002; Yamagishi et al., 2005).

Oceans emit more than 25% of natural produced N_2O and contribute significantly to the global N_2O budget (Prather et al., 2001; Seitzinger et al., 2000). Particularly coastal regions, including estuarine and upwelling regions, play a major role for the formation and release of N_2O to the atmosphere (Bange et al., 1996; Naqvi et al., 2000; Seitzinger et al., 2000). In the Baltic Sea, first investigations were made by Rönner (1983) who found the Baltic Sea to be a source of atmospheric N_2O. In contrast to open ocean areas coastal regions are expected to be more influenced by conversion processes in sediments or by riverine inputs. In the Bodden waters and Danish fjords of the Baltic Sea enhanced N_2O concentrations were correlated with seasonal riverine input (Jørgensen and Sørensen, 1985; Dahlke et al., 2000). Additionally, denitrification processes in sediments were shown to contribute to the release of N_2O in Danish fjords (Jørgensen and Sørensen, 1985).

1.2 Study area

Samples of dissolved N_2O were measured at 26 stations in the western, southern and central Baltic Sea. The cruise took place on board the German research vessel Gauss (expedition no. 11/03/04) from 13 October to 25 October 2003 as part of the Cooperative Monitoring in the Baltic Sea Environment (COMBINE) program of the Baltic Marine Environment Protection Commission (Helsinki Commission, HELCOM, see http://www.helcom.fi). The locations of sampled stations are shown in Fig. 1.

The Baltic Sea is an adjacent sea of the Atlantic Ocean and part of the European continental shelf. It consists of a series of basins (Arkona, Bornholm, and Gotland Basin; see Fig. 1), with restricted horizontal and vertical water exchange due to shallow sills and a clear salinity stratification of water masses.

In January 2003 a major inflow of cold, highly saline and oxygen-rich North Sea Water was observed. It was the most important inflow event since 1993 and terminated

the ongoing stagnation period in the central Baltic Sea (Feistel et al., 2003; Nausch et al., 2003). This inflow event was preceded by a minor inflow of warmer and less oxygenated water in August 2002. Due to the inflow of North Sea Water oxygen conditions changed from anoxic to oxic in most parts of the Baltic Sea. From the inflow in January 2003 until our cruise in October 2003 water renewal was already detectable at the Farö Deep (# 286), however the western Gotland Basin was still unventilated (Feistel et al., 2003; Nausch et al., 2003).

Due to the fact that N_2O production highly depends on environmental conditions such as e.g. oxygen concentration (e.g., Naqvi et al., 2000) any natural or anthropogenic-induced shifts of coastal ecosystems will modulate the formation and subsequent release of N_2O to the atmosphere. In this context the inflow of North Sea Water into the Baltic Sea offered a good opportunity to investigate naturally changing environmental conditions with regard to the production of N_2O.

1.3 Definition of water masses

We refer to four different water masses, characterized by temperature, salinity and oxygen concentrations (Fig. 2). The definition of water masses follows the description of the "Institut für Ostseeforschung" (IOW) cruise reports (Nausch, 2003a, b, c; Nagel, 2003; Feistel, 2003; Wasmund, 2003) and the hydrographic-chemical report of the Baltic Sea in 2003 (Nausch et al., 2004). These water masses were characteristic for the time period after the inflow event in summer and autumn 2003.

The Surface Water layer (sw) was characterized by uniform temperature and salinity, in combination with high oxygen concentrations. Below this layer, rapidly decreasing temperatures indicated Winter Water (ww), which is formed annually during convection in winter. Salinity and oxygen concentrations were still uniform. The "old" Bottom Water (bw) was visible by increasing temperature and simultaneously increasing salinity. In this water mass, located below the Winter Water, oxygen concentrations decreased rapidly, to anoxic conditions at some stations. A permanent halocline between Winter Water and Bottom Water strongly restricts the vertical exchange and is the reason for

the development of stagnant deep waters with oxygen depletion up to anoxia accompanied by accumulation of hydrogen sulphide (H_2S). Bottom Water, affected by the North Sea Water inflow in January 2003 (abw) was characterized by decreasing temperature and enhanced oxygen concentrations compared to previous Bottom Water (bw) values. Due to its higher density the affected Bottom Water lifts up the "old" Bottom Water.

2 Methods

Water samples were taken using a combined Seabird SBE911 CTD and Hydrobios rosette sampler equipped with 13 free-flow bottles. Samples for N_2O analysis were collected in triplicate from various depths. The analytical method applied was a modification of the method described by (Bange et al., 2001). Bubble free samples were taken immediately following oxygen sampling from the rosette in 24 mL glass vials, sealed directly with butyl rubber stoppers and crimped with aluminium caps. To prevent microbial activity, samples were poisoned with 500 μL of a 2 mM mercury chloride solution.10 mL of the sample were then replaced with a helium headspace for each vial, and the samples were equilibrated for at least two hours at room temperature (temperature was recorded continuously). A 9 mL subsample from the headspace was used to flush a 2 mL sample loop after passing through a moisture trap (filled with Sicapent®, Merck Germany). Gaschromatographic separation was performed at 190°C on a packed molecular sieve column (6 ft × 1/8″ SS, 5 A, mesh 80/100, Alltech GmbH, Germany). The N_2O was detected with an electron capture detector. A mixture of argon with 5 percent by volume methane was used as carrier gas with a flow of 21 mL min^{-1}. For the two-point calibration procedure we used standard gas mixtures with 311.8±0.2 ppb and 346.5±0.2 ppb N_2O in synthetic air (Deuste Steininger GmbH, Mühlhausen Germany). The standard mixtures have been calibrated against the NOAA (National Oceanic and Atmospheric Administration, Boulder, Co.) standard scale in the laboratories of the Air Chemistry Division of the Max Planck Institute for

Chemistry, Mainz, Germany.

2.1 Calculations

N_2O water concentrations (C_{N2O}) were calculated as follows:

$$C_{N2O}\left[\text{nmol}\,L^{-1}\right] = (\,\beta \text{ x } P\, V_{wp} + \frac{\text{x } P}{R\,T}\, V_{hs}\,)\;/\;V_{wp} \quad (1)$$

where β stands for the Bunsen solubility in nmol L^{-1} atm^{-1} (Weiss and Price, 1980), x is the dry gas mole fraction of N_2O in the headspace in ppb, P is the atmospheric pressure in atm, V_{wp} and V_{hs} stand for the volumes of the water and headspace phases, respectively. R is the gas constant (8.2054 10^{-2} L atm mol^{-1} K^{-1}) and T is the temperature during equilibration. The salinity was measured by the CTD-Sensor during water sample collection; the temperature was measured while subsampling the headspace of the sample vial (i.e. the equilibration temperature). The overall relative mean analytical error was estimated to be ±1.8%.

The excess N_2O (ΔN_2O) was calculated as the difference between the calculated N_2O equilibrium concentration and the measured concentration of N_2O as follows

$$\Delta N_2O\ (\text{nmol}\ L^{-1}) = N_2O\ (\text{observed}) - N_2O\ (\text{equilibrium}). \quad (2)$$

Since the water masses in the Baltic Sea are comparably young (e.g. 11 years for the oldest bottom water at the Landsort Deep) (Meier, 2005) it is reasonable to calculate the equilibrium value with the actual atmospheric N_2O mole fraction. During the cruise we measured a mean of 318 ppb (±3 ppb, n=84) in the atmosphere, which is in good agreement with the monthly mean of 318.5±0.2 ppb in October 2003 measured at Mace Head, Ireland. This value was taken from the Advanced Global Atmospheric Gases Experiment (AGAGE) data set (updated version from May 2005, available at ftp://cdiac.esd.ornl.edu (subdirectory pub/ale_gage_Agage/Agage/gc-md/monthly) at the Carbon Dioxide Information Analysis Center in Oak Ridge, Tennessee).

The apparent oxygen utilization (AOU) was calculated as follows:

$$\text{AOU}\ (\mu\text{mol L}^{-1}) = \text{O}_2\ (\text{equilibrium}) - \text{O}_2\ (\text{observed}). \quad (3)$$

The equilibrium values of dissolved oxygen (O_2) were calculated with the equation given by Weiss (1970). The concentration of H_2S is expressed as the negative oxygen equivalent ($1\,\mu\text{mol L}^{-1}$ $H_2S = -2.00\,\mu\text{mol L}^{-1}$ O_2). Dissolved nutrients and CTD data were provided by the participating working groups.

The N_2O inventory of single basins m_{N2O} was calculated as follows:

$$m_{N2O}\ [\text{tons}] = \bar{C}_{N2O} \times n_{N2O} \times V \times 10^{-3} \quad (4)$$

where $\bar{C}_{N2O}$ is the mean measured N_2O concentration in the single basins from the upper part of the halocline to the bottom (nmol L^{-1}), n_{N2O} is the mole weight of N_2O ($44\,\text{g mol}^{-1}$) and V is the water volume of the single basins (km^3).

The water volumes are based on data published in Sect. 4.4.1 (HELCOM, 1996), available at: http://www.vtt.fi/inf/baltic/balticinfo/index.html.

The N_2O content of basins was calculated with data of the following stations: Bornholm Basin: station 140, 200, 213, 222, eastern Gotland Basin: station 250, 259, 260, 272, western Gotland Basin: station 240, 245, 284. Station 286 is located in the northern part of the Gotland Basin and thus has not been taken into account.

Nitrification rates (N) were estimated for the Bornholm Basin and the eastern Gotland Basin.

$$\text{N}\left[\text{nmol L}^{-1}\ \text{d}^{-1}\right] = \frac{\Delta m_{N2O}}{d_{\text{basin}} \times V_{\text{basin}} \times n \times 10^{-9}} \times r_{N2O} \quad (5)$$

where Δm_{N2O} is the difference of calculated N_2O content of the basins before and after the inflow event in tons, d_{basin} is the number of days from the first observation of the intrusion of North Sea Water until our measurements (assumed by data of the cruise reports of Nausch, 2003a, b, c; Nagel, 2003; Feistel, 2003; Wasmund, 2003).

V_{basin} is the calculated volume of the basins (km^3) (based on data published in Sect. 4.4.1 (HELCOM, 1996), available at: www.vtt.fi/inf/baltic/balticinfo/index.html), n

is the mole weight of N_2O (44 g mol^{-1}), and r_{N2O} is the assumed N_2O release of 0.3% in continental shelves during nitrification (Seitzinger and Kroeze, 1998).

3 Results

In order to account for the hydrographic characteristics of the Baltic Sea and the direction of the inflow of North Sea Water, we present the results according to the following classifications: I) well-mixed basins such as the Kiel, Lübeck and Pomeranian Bights and II) clearly stratified basins such as the Arkona, the Bornholm, the western and the eastern Gotland Basin (see Fig. 2). For each basin selected profiles are shown.

3.1 Well-mixed basins

At shallow stations, with depths <30 m (station 10, 12, 22, 30, 41, 46, 121, 130, 133, 360, OB Boje, OB 4, Fig. 1), water masses were well mixed, and profiles showed nearly uniform vertical distributions of all parameters (Fig. 3a). Concentrations of N_2O were near equilibrium; however the Pomeranian Bight (station 130, 133, OB Boje, OB 4) showed enhanced saturation values (104.6±7.9%) in comparison with the Kiel Bight (station 360) and the Lübeck (station 22) and Mecklenburg Bight (station 10, 12, 41, 46; 79.3±10.7%). No correlations were found between ΔN_2O and other parameters like O_2 and NO_3^- (Figs. 3b–c).

3.2 Stratified basins

Basins with water depths >30 m (Figs. 4–7) were clearly stratified into layers of well mixed Surface Water (sw), Winter (ww) and Bottom Water (bw) as described above. At several stations Bottom Water was affected by North Sea Water (abw), up to the Farö Deep in the northern part of the central Baltic Sea (Fig. 1, station 286) (Feistel et al., 2003). However, below 110 m the deep water of the Farö Deep was still anoxic, though

with decreasing H_2S concentrations from 125 m to the bottom (Fig. 6a, lower profiles). Stations in the western Gotland Basin such as the Landsort Deep (station 284, Fig. 7a) or the Karlsö Deep (station 245, not shown) were still unaffected by the inflow event, thus below 80 m H_2S concentrations were uniform.

3.2.1 Arkona Basin

In the Arkona Basin (stations 109 and 113 (Fig. 4a)), N_2O concentrations were constant and near equilibrium (10.9±0.7 nmol L^{-1}) throughout the water column. In the Winter Water below the thermocline at 15 m O_2 concentrations decreased, associated with increasing NO_2^-, NO_3^- and NH_4^+. ΔN_2O was slightly negatively correlated with O_2(Fig. 4b), and positively correlated with NO_3^- (Fig. 4c). At the bottom below 40 m inflowing North Sea (arrow in Fig. 4a) water formed a 5 to 10 m thick oxygen enriched layer, however with no clear influence on the N_2O concentration.

3.2.2 Bornholm Basin

In the Bornholm Basin (Fig. 5, stations 140, 200, 213 and 222), N_2O profiles in the central basin (stations 200 (not shown) and 213 (Fig. 5a)) can be clearly distinguished from stations where water flows into and out of the basin. At station 140 (inflow, not shown) concentrations and distribution of N_2O and ΔN_2O were comparable to the Arkona Basin. At station 222 (outflow, not shown) N_2O concentrations in the surface layer were uniform near equilibrium at approximately 10 nmol L^{-1}, below the surface layer concentrations were uniform around 15.4 nmol L^{-1}. In the central Bornholm Basin, at station 200 (not shown) and 213 (Fig. 5a) N_2O concentrations increased rapidly within the layer affected by North Sea Water (abw, below 60 m), with N_2O values up to 31.3 nmol L^{-1} (station 200). These were the highest values measured during the entire cruise. In water masses above, N_2O was near equilibrium, with slightly enhanced ΔN_2O values in the "old" Bottom Water (bw, 40–60 m). In the Bornholm Basin ΔN_2O was clearly negatively correlated with oxygen and positively with NO_3^- (Fig. 5b–c), how-

ever, both correlations were nonlinear and were fitted best by polynomials.

3.2.3 Eastern Gotland Basin

The situation became more complex in the eastern Gotland basin (stations 259, 250, 260, 271 and 286). Profiles were not as homogeneous as in the Arkona or Bornholm Basin. Again, N_2O concentrations were near equilibrium in the surface layer (sw, 0–20/30 m) and the Winter Water (ww, 20/30–60 m). At station 271 (Fig. 6a, upper profiles) the Bottom Water (bw) was completely oxygenated, with N_2O values at approximately 20 nmol L^{-1} and positive ΔN_2O. At station 286 (Fig. 6a, lower profiles) the Bottom Water (bw) was affected by the North Sea Water too, but was still anoxic. Inflow of North Sea Water was detectable by decreasing H_2S concentrations down to the bottom. Throughout the Bottom Water N_2O concentrations remained near zero. At station 250 (not shown), 271 (Fig. 6a, upper profiles) and 286 (Fig. 6a, lower profiles) a sharp local minimum of N_2O concentrations was observed at depths between 90 and 110 m (see arrows in Fig. 6a), combined with a local minimum in NO_3^- values. Except for the anoxic water masses, ΔN_2O was linearly correlated with O_2 and NO_3^- (Fig. 6b–c).

3.2.4 Western Gotland Basin

The western Gotland Basin with stations 284 (Fig. 7a), 245 and 240 revealed the "old" conditions, showing characteristics as yet unaffected by the latest intrusion of oxic North Sea Water. N_2O in the surface layer (sw, 0–20/40 m) and Winter Water (ww, 20/40–60 m) was near equilibrium. Below 50 m, oxygen concentrations decreased rapidly and N_2O concentrations dropped sharply within the oxic/anoxic interface and remained near zero in the anoxic deep waters. ΔN_2O values were negative and were not correlated with NO_3^- (Fig. 7c). ΔN_2O was logarithmically correlated with oxygen (Fig. 7b).

3.3 Estimated contribution of the North Sea Water inflow to the production of N_2O

The North Sea Water inflow consisted of a water volume of 200 km^3 (Feistel and Nausch, 2003). With an assumed N_2O concentration of 10±2 nmol L^{-1} (Law and Owens, 1990), the North Sea Water transported approximately 88±18 tons N_2O into the Baltic Sea.

Before the North Sea Water inflow, the deep waters below the halocline were anoxic, not only in the western but also in the eastern Gotland Basin and the Bornholm Basin (Schmidt, 2002). Thus, N_2O concentrations near zero similar to measured profiles in the western Gotland Basin in October 2003 (Fig. 7a) can be assumed. This is supported by the drop in concentration at station 286 (Fig. 7a, lower profile), which is assumed to be related to the previously anoxic bottom water. The mean N_2O concentration in the western Gotland Basin was 0.97±0.34 nmol L^{-1}, on the basis of these values the calculated N_2O content of the Bornholm Basin and the eastern Gotland Basin was approximately 64±23 tons before the inflow (Table 1).

After the inflow event the Bornholm Basin and the eastern Gotland Basin are clearly influenced by the North Sea Water, whereas the western Gotland Basin was still unaffected (Nausch, 2003a, b, c; Nagel, 2003; Feistel, 2003; Wasmund, 2003). The N_2O content of the Bornholm Basin and the eastern Gotland Basin, calculated with the mean of measured N_2O concentrations below the halocline in these basins, was about 1194±256 tons (Table 1).

4 Discussion

Over the past two decades the previously frequent inflows of North Sea Water became rather rare (Feistel and Nausch, 2003), and oxygen levels in deep waters decreased. Thus, oxygen conditions in the Baltic Sea deep water cover a continuum from almost permanently oxic (i.e. Arkona Basin) to almost permanently anoxic conditions (i.e. western Gotland Basin), with changes at non-regular intervals between anoxic and

oxic (i.e. Bornholm Basin, eastern Gotland Basin) (Feistel, 2003; Nausch, 2003a, b, c; Nagel, 2003; Wasmund, 2003).

The inflow event in January 2003 rapidly changed the environmental conditions of the deep basins. With respect to the oxygen dependent production of N_2O, our measured N_2O concentrations reflect the continuum of unaffected and changing oxygen conditions quite well. In oxic and well mixed waters, vertical N_2O profiles were homogenous, with concentrations near equilibrium (Fig. 3a). Anoxic deep water layers, unaffected by North Sea Water (i.e. in the western Gotland Basin), had N_2O concentrations near zero (Fig. 7a). Therefore, in both cases no correlations between N_2O and either oxygen or nitrate were found (Figs. 3b–c, Figs. 7b–c). In contrast, stratified and recently ventilated water bodies in the Bornholm and eastern Gotland Basin revealed N_2O distributions that were clearly correlated with oxygen and nitrate (Figs. 5b–c, Figs. 6b–c).

These vertical N_2O distributions are in general agreement with the few previously published N_2O profiles from the central Baltic Sea (Rönner, 1983; Rönner and Sörensson, 1985; Brettar and Rheinheimer, 1992). However, the past environmental settings of the deep central Baltic Sea basins were different: N_2O profiles from the central Baltic Sea reported by (Rönner, 1983) were measured when oxic conditions prevailed during August–September 1977 after a strong inflow event in 1976/1977 (Schinke and Matthäus, 1998). Their N_2O profiles are comparable to our profiles, measured in the completely oxygenated Bornholm Basin during October 2003 (Fig. 5a). Anoxic conditions were re-established in July 1979 and May–June 1980. The shape of the N_2O profiles from the then anoxic Gotland Deep, measured by Rönner and Sörensson (1985) is comparable to the N_2O profiles measured in the western Gotland Basin (e.g., the Landsort Deep, Fig. 7a). This is the same for profiles measured by Brettar and Rheinheimer (1991) in August 1986 and July 1987 during the 1983–1993 stagnation periods (Schinke and Matthäus, 1998).

In the following sections we discuss the processes that may cause the observed distributions of N_2O in the different basins.

4.1 Non-biological aspects

In surface layers and well-mixed water bodies of shallow stations, observed N_2O concentrations were near the equilibrium due to exchange with the atmosphere. In the Winter Water N_2O concentrations were also near equilibrium, however with higher absolute values than in the surface layer (see Figs. 5a–7a). Mainly hydrographic aspects were here responsible for the observed N_2O distribution. This water mass is formed during winter convection, when N_2O concentrations were in equilibrium with the atmosphere and this signal is conserved during stratification of the upper layer in summer. The lower temperature and hence higher N_2O solubility during formation of the Winter Water are the reason for the enhanced N_2O concentrations in this layer.

A non-biological factor affecting N_2O in the deep water of the Baltic Sea might be advection with inflowing North Sea Water. Intrusion of N_2O by North Sea Water should be detectable at stratified stations, where the inflow of North Sea Water was clearly identified. In the Arkona Basin (station 109 and 113) this inflow was detectable at the bottom by lower temperature and higher oxygen concentrations; however, N_2O concentrations did not increase and remained close to equilibrium (Figs. 4a–b). These results point to only low advection of N_2O by North Sea Water, and are supported by measurements of (Law and Owens, 1990). They found N_2O concentrations close to equilibrium up to approximately 10 nmol L^{-1} in the North Sea. Thus, the enhanced N_2O values detected in layers affected by North Sea Water, for example in the Bornholm Basin (station 200 and 213), must originate from biological in situ production since the inflow, rather than advection.

4.2 Biological aspects

Previous studies demonstrated the existence of N_2O producing bacteria and investigated the biological pathways, namely nitrification and denitrification in the Baltic Sea (Bauer, 2003; Brettar and Höfle, 1993; Brettar et al., 2001). Both processes are commonly inferred by correlations between N_2O and oxygen or nitrate (Yoshinari, 1976;

Yoshida et al., 1989; Cohen and Gordon, 1978; Butler et al., 1989).

4.2.1 Anoxic waters

In general, in anoxic and H_2S containing bottom waters N_2O concentrations were constantly near zero, and therefore no correlation with either O_2 or NO_3^- was found. The N_2O production by nitrification and denitrification might probably be inhibited by the presence of H_2S (Joye and Hollibaugh, 1995; Knowles, 1982; Sørensen et al., 1980), and while changing to anoxic conditions, N_2O can be consumed during denitrification as an electron acceptor instead of oxygen (Elkins et al., 1978; Cohen and Gordon, 1978). However, in contrast to other authors (Rönner et al., 1983; Brettar and Rheinheimer, 1992) we found low and uniformly distributed concentrations of N_2O (up to 1.7 nmol L^{-1}) in the anoxic water masses, which may have been residuals of a previous production process during oxic conditions.

4.2.2 Suboxic waters

In suboxic waters and at the boundary to anoxic water masses N_2O is expected to be mainly produced by denitrification processes (Codispoti et al., 2001), usually indicated by decreasing NO_3^- concentrations and a secondary NO_2^- peak (Wrage et al., 2001; Kristiansen and Schaanning, 2002). These indicators for denitrification were found only at the Farö Deep (station 286, 90 m). However, no accumulation of N_2O was observed, rather a local minimum of N_2O was found (Fig. 6a, indicated by arrows). Hannig et al. (2005) investigated denitrification associated microorganisms in the Gotland Basin (station 271 and 286) in October 2003. They did not find denitrification activities in suboxic water masses, but a high denitrifying potential restricted to a narrow depth range at the oxic-anoxic interface and the sulfidic zone. However, in these depths an accumulation of N_2O was not found either.

The local minimum of N_2O was observed not only at the Farö Deep, but also at the Gotland Deep (Fig. 6a, indicated by arrows) and station 250 (profile not shown). A

residual signal of the small inflow event in August 2002 could be observed at these depths between 90 and 110 m (Feistel et al., 2003). We assume that this minimum of N_2O is a previous signal of former anoxic bottom water, pushed up by the small inflow event in August 2002. The restriction of denitrification activity to a narrow depth range at anoxic-oxic boundaries was not only reported by Hannig et al. (2005) but also by Brettar et al. (2001). Therefore, the lack of denitrification signals leads to the question, which processes might cause the measured N_2O concentrations.

4.2.3 Correlation between N_2O and O_2

In general, in oxic waters N_2O is positively correlated with nitrate, negatively with oxygen, indicating a production by nitrification. However, below a distinct threshold of oxygen concentration a clear inversion of relationship was found. Figure 8 shows the correlation between ΔN_2O and O_2 in the Baltic Sea. At O_2 concentrations $>50\,\mu mol\,L^{-1}$ ΔN_2O is clearly negatively correlated with O_2, indicating production by nitrification (see Fig. 8, green data points). At O_2 concentrations $<20\,\mu mol\,L^{-1}$ ΔN_2O and O_2 were significantly positively correlated (see Fig. 8, red data points), data between $20\,\mu mol\,L^{-1}$ and $50\,\mu mol\,L^{-1}$ were extremely scattered (see Fig. 8, black data points).

These findings suggest a change in N_2O converting processes. Particularly in environments with rapidly changing conditions it is advantageous for microorganisms to be able to switch between different metabolic pathways. The change between aerobic and anaerobic metabolism and thus the yield of N_2O during these processes is probably controlled particularly by the O_2 concentration, although little is known about the detailed mechanisms (Baumann et al., 1996; John, 1977; Sørensen, 1987). Our results suggest a production of N_2O during nitrification until an oxygen threshold of around $20–50\,\mu mol\,L^{-1}$, whereas the exact concentration is not to be determined due to the scattered data. Below this threshold N_2O seemed to be degraded; probably used as an electron acceptor instead of oxygen and thereby reduced to N_2 (Elkins et al., 1978; Cohen and Gordon, 1978). In the literature, threshold values of $2\,\mu mol\,L^{-1}$ for nitrification

are reported (Carlucci and McNally, 1969; Gundersen et al., 1966). For several nitrifiers the ability to switch between "classical" nitrification, nitrifier-denitrification and aerobic denitrification was shown (Wrage et al., 2001; Whittaker et al., 2000; Zart et al., 2000; Zehr and Ward, 2002). The oxygen sensitivity is species-specific and also enzyme-specific; therefore the scatter of data might reflect the variety of involved species and enzymes (Jiang and Bakken, 2000; Goreau et al., 1980; Wetzel, 1983; Robertson et al., 1988; Richardson, 2000). Bauer (2003) investigated NH_4^+ oxidizing bacteria in the eastern Gotland Basin, and found similar bacterial communities at different depths; their nitrification activities however depended on O_2 concentrations.

Therefore, the ability of nitrifiers to perform denitrifying processes and the lack of "classical" denitrifying signals, a switch of N_2O producing processes by nitrifiers can be assumed. These findings are in agreement with the assumptions of Rönner (1983), who also assumed, that nitrification is the main N_2O production pathway in the Baltic Sea.

Alternatively, it is also possible to interpret the data from the hydrographical or temporal point of view. Figure 9 shows the same data set as shown in Fig. 8. This time the data set is grouped not according to the oxygen concentrations but to the affiliation to different basins. Station 286 was excluded due to its transitional character. At this station anoxic conditions in the deep waters were found similar to other stations in the western Gotland Basin, but H_2S concentrations were decreasing towards the bottom. This indicates beginning ventilation, however still too weak to lead to oxic conditions.

In the stratified basins such as the Bornholm Basin, and the eastern and western Gotland Basin correlations of ΔN_2O and O_2 were regionally different and not always linear (Figs. 5b–c, 6b–c, 7a, 9). Particularly in the Bornholm Basin, N_2O and oxygen as well as N_2O and nitrate showed significant non-linear relationships (Figs. 5b–c, 9). The Bornholm Basin, which was anoxic before the inflow (Schmidt, 2002), was ventilated by North Sea Water in January 2003, months before the northern part of the eastern Gotland Basin was affected by the inflow (Nausch, 2003a; Nausch et al., 2004). In October 2003 the oxygen conditions were already switching back to suboxic condi-

tions (Nausch, 2003c; Wasmund, 2003), visible by decreasing oxygen concentrations compared to the beginning of the year. Accordingly the duration of elevated oxygen concentration in the respective basins may contribute to the observed accumulation of N_2O. In the eastern Gotland Basin (Figs. 6b–c, 9) the anoxic conditions changed a few months after the Bornholm Basin: the Gotland Deep was ventilated by North Sea Water in May 2003 (Nausch, 2003b). Thus, there was less time for N_2O accumulation. For various communities of NH_4^+ oxidizing bacteria different lag times after switching from anoxic to oxic incubations were shown and the production of N_2O might not have started directly after the ventilation by North Sea Water (Bodelier et al., 1996). In the western Gotland Basin (Figs. 7b–c, 9) no ventilation by North Sea Water had occurred by October 2003, therefore degradation of N_2O at the oxic-anoxic interface was found. We suspect that the correlation between ΔN_2O and O_2 in the Bornholm Basin and the eastern Gotland Basin will become similar to those of the western Gotland Basin with time, when the conditions change to anoxic.

Summarizing, we assume a conversion of N_2O mainly by nitrifiers, depending on oxygen concentration and with significant spatial and temporal characteristics.

4.3 Estimated contribution of the North Sea Water inflow to the production of N_2O

The estimated N_2O content in the stratified basins showed distinctly higher values after the inflow of the North Sea Water than before. The N_2O concentration in the North Sea Water was assumed to be near equilibrium, so there was no significant advection of N_2O from the North Sea. Thus, the observed elevated N_2O concentrations in the Baltic Sea basins result from a stimulation of N_2O production by the inflow, most likely by advection of oxygen (see Table 1).

Although more than 1000 tons of N_2O were produced, it is questionable whether the North Sea Water inflow makes the Baltic Sea a source of atmospheric N_2O. Due to the strong salinity stratification, it can be assumed that the formed N_2O stays below the permanent halocline, and therefore it will not reach the atmosphere. Commonly N_2O budgets were modelled as a function of nitrification and denitrification. Seitzinger and

Kroeze (1998) modelled the distribution of N_2O production, amongst others based on the input of nitrogen compounds into estuaries by rivers. However, estimations of global N_2O emissions do not or only to a small extent take into account the hydrographic aspects. The stratification of the water column probably lead to a reduced release of calculated amounts, and accordingly to an overestimation of N_2O emissions.

The assumption of remaining N_2O below the halocline leads to the question, whether and to what extent the nitrogen cycle might be influenced.

Based on the calculated N_2O content of the basins and the assumption of nitrification as the main production pathway N_2O production rates and nitrification rates were estimated (Table 2). These nitrification rates are in good agreement with previously published rates for the Baltic Sea (Enoksson, 1986; Bauer 2003). Bauer (2003) calculated for the eastern Gotland Basin mean nitrification rates of 21.6±11.1 nmol L^{-1} at 60 m depth, respectively 44.3±33.1 nmol L^{-1} at 100 m depth.

These rates are comparably low (e.g. Bianchi et al., 1999); therefore the influence on the nitrogen cycle in the Baltic Sea might be small, too. N_2O might play a minor role as a reserve- or buffer-molecule during the change to anoxic conditions, preserving nitrifying processes in exchange for oxygen for a short while.

5 Conclusions

In January 2003 a major inflow of cold, highly saline and oxygen-rich North Sea Water was observed, terminating the ongoing stagnation period in parts of the central Baltic Sea.

- In agreement with previous studies, we found N_2O production mainly in oxic water masses below the Winter Water layer.
- We found no indication for advection of N_2O by North Sea Water; however, the environmental conditions for N_2O production were clearly changed due to the North Sea Water inflow.

– The inflow leads to a stimulation of N_2O production below the permanent halocline, but due to the halocline, the Baltic Sea is not a significant source of N_2O to the atmosphere.

– There was no indication for an accumulation of N_2O during denitrification. In oxic and suboxic water masses nitrification seems to be the main production pathway. The occurrence of nitrifier-denitrification and aerobic denitrification is possible, but needs further investigations.

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Table 1. Estimated N_2O content of single basins in the Baltic Sea below the halocline, before and after the inflow of North Sea Water in January 2003.

	mean N_2O conc. below the halocline (nmol L^{-1})	Water volume (km^3)	N_2O content before the inflow event (tons)	N_2O content after the inflow event (tons)
Bornholm Basin	>50 m 16.59±5.61	306	13±5	223±76
eastern Gotland Basin	>70 m 18.46±3.43	1195	51±18	971±180
Σ		1501	**64±23**	**1194±256**
western Gotland Basin	>70 m 0.97±0.34	657	28±10	28±10

Table 2. Estimated nitrification rates in the Bornholm Basin and the eastern Gotland Basin, based on the assumption of 0.3% N_2O release during nitrification (Seitzinger and Kroeze, 1998).

	Δm_{N2O} (tons)	d_{basin} (day)	Water volume (km^3)	N_2O production rate (nmol L^{-1} d^{-1})	nitrification rate (nmol L^{-1} d^{-1})
Bornholm Basin	220±81	265	306	0.059±0.023	19.62±7.57
eastern Gotland Basin	920±198	167	1195	0.105±0.021	34.92±6.87

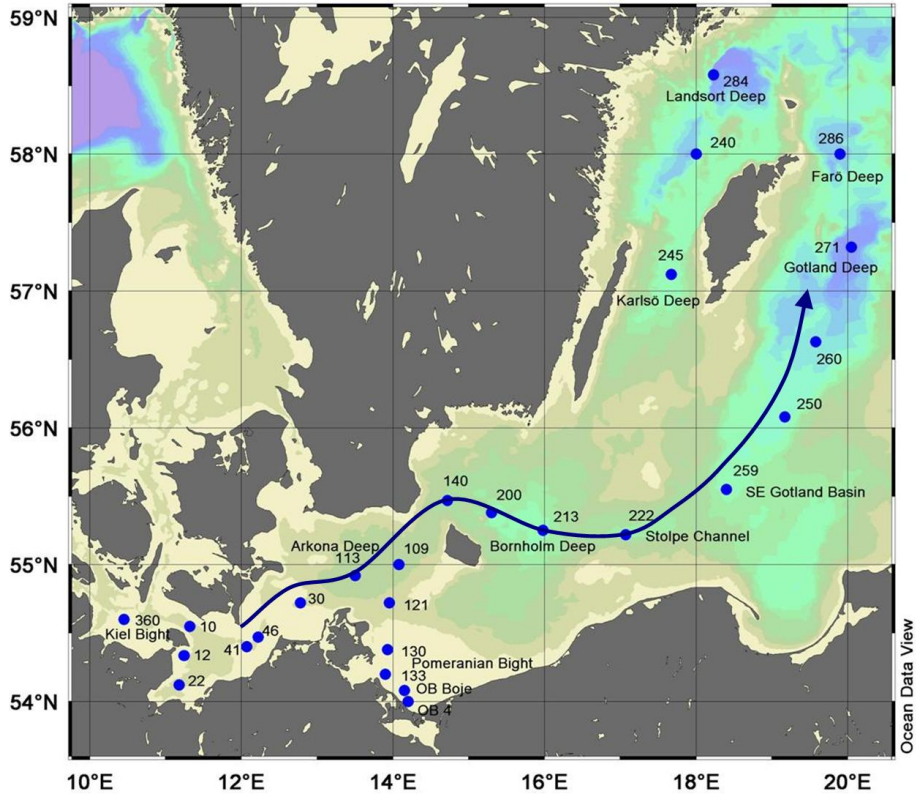

Fig. 1. Map of the western, southern and central Baltic Sea with locations of the stations. The stations were grouped as follows: well-mixed stations are number 10, 12, 22, 30, 41, 46, 121, 130, 133, 360, OB Boje and OB 4; the Arkona Basin is represented by station 109 and 113; the Bornholm Basin is represented by station 140, 200, 213 and 222; in the eastern Gotland Basin station 250, 259, 260, 271 and 286 were grouped; and the western Gotland Basin is represented by station 240, 245 and 284. The arrow indicates the main flow direction of North Sea Water.

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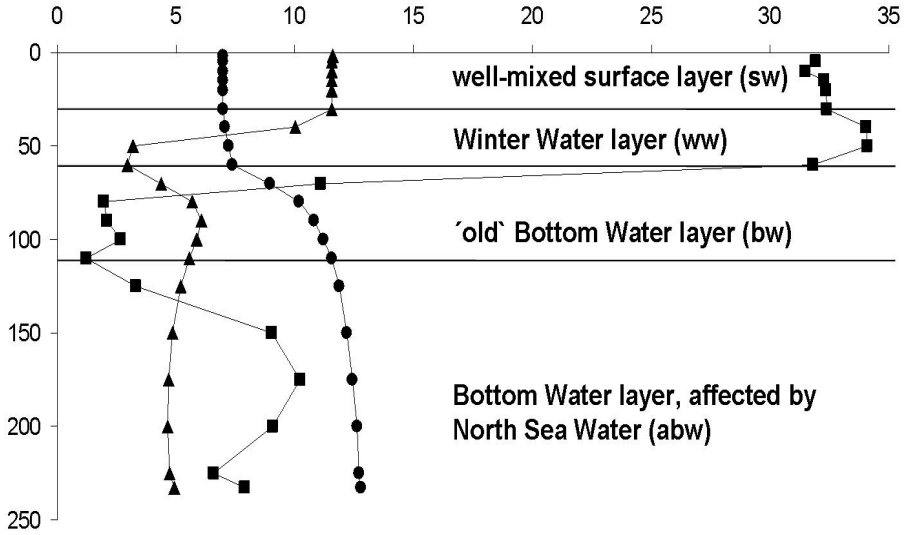

Fig. 2. Characterization of different water masses in the Baltic Sea, for example at station 271 in the Eastern Gotland Basin (triangles: temperature (°C), circles: salinity, squares: oxygen (μmol 10^1 L^{-1}).

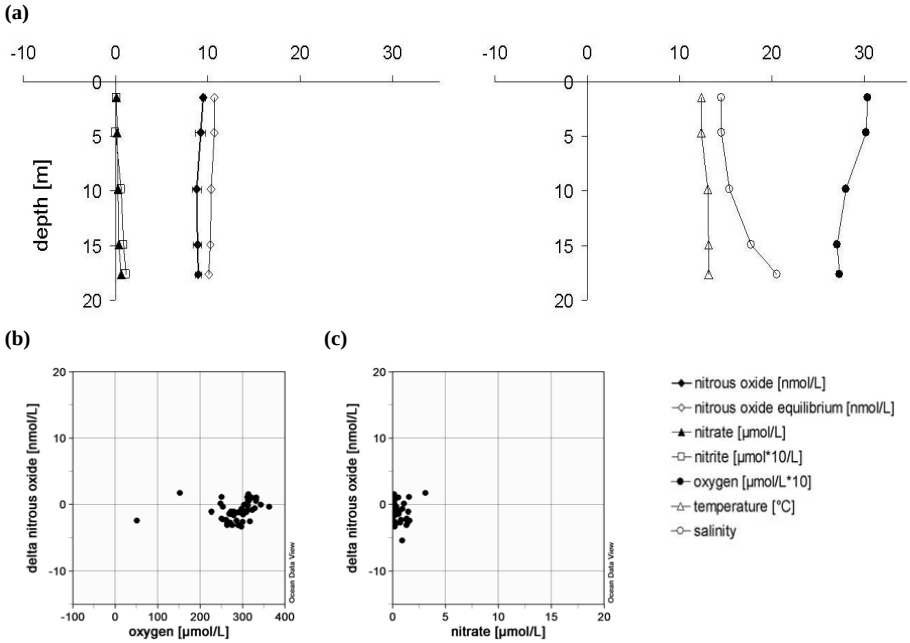

Fig. 3. Well mixed basins; **(a)** left plot with profiles of N_2O, calculated N_2O equilibrium concentration, NO_3^-, NO_2^- at station 41 in the Mecklenburg Bight and right plot with profiles of temperature, salinity and oxygen at station 41 in the Mecklenburg Bight; **(b)** ΔN_2O plotted against oxygen at all stations <30 m; **(c)** ΔN_2O plotted against NO_3^- at all stations <30 m.

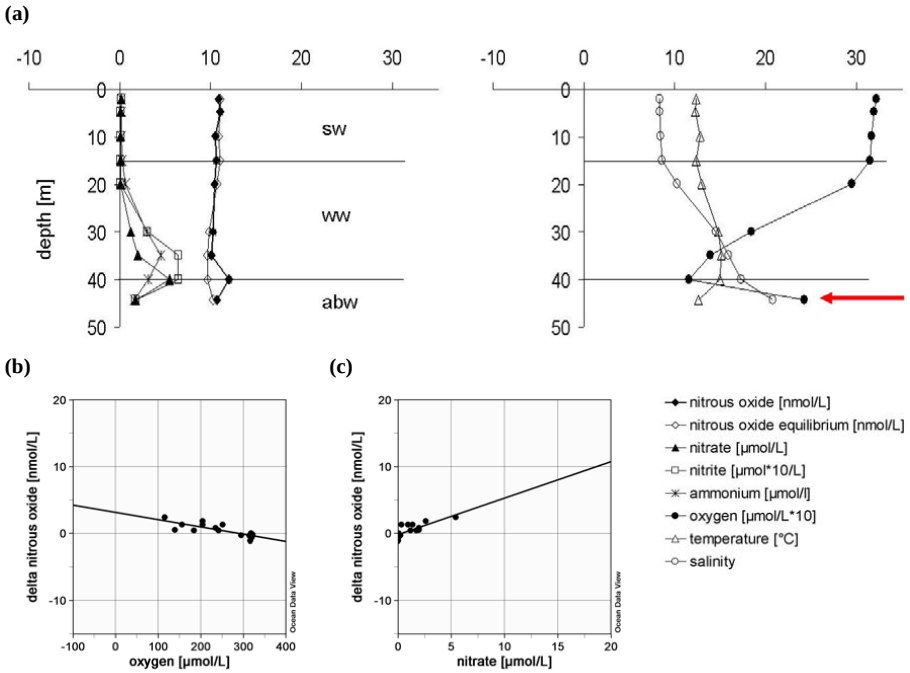

Fig. 4. Arkona Basin; **(a)** station 113 (Arkona Deep): left plot with profiles of N_2O, N_2O equilibrium concentration, NO_3^-, NO_2^-, right plot with profiles of temperature, salinity and oxygen, the arrow indicates the influence of North Sea Water; abbreviations see Fig. 2.; **(b)** ΔN_2O plotted against oxygen (at all stations in the Arkona Basin, $y=-0.011\ x+3.132$, $R^2=0.67$); **(c)** ΔN_2O plotted against NO_3^- (at all stations in the Arkona Basin, $y=0.546\ x-0.807$, $R^2=0.66$).

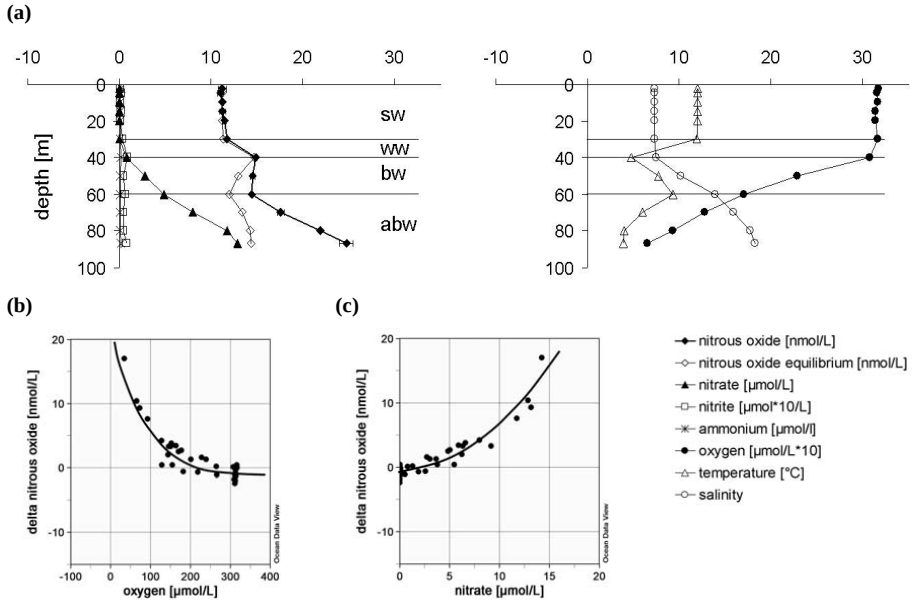

Fig. 5. Central Bornholm Basin; **(a)** station 213 (Bornholm Deep): left plot with profiles of N_2O, N_2O equilibrium concentration, NO_3^-, NO_2^-, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; **(b)** ΔN_2O plotted against oxygen (at all stations in the Bornholm Basin, $y=0.0003\ x^2-0.1531\ x+19.517$, $R^2=0.88$); **(c)** ΔN_2O plotted against NO_3^- (at all stations in the Bornholm Basin, $y=0.0585\ x^2+0.1438\ x-0.6155$, $R^2=0.90$).

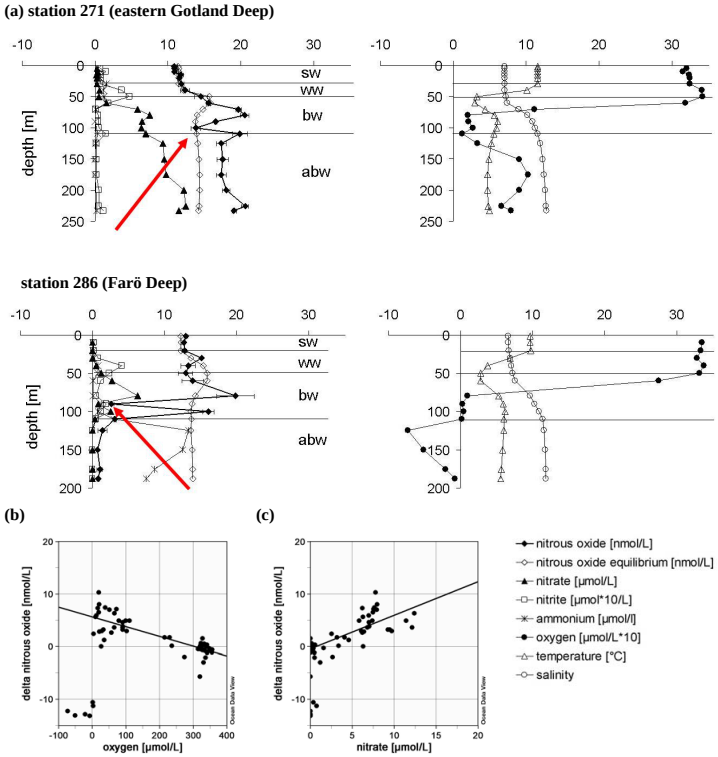

Fig. 6. Eastern Gotland Basin; **(a)** station 271 (Gotland Deep, upper plots) and 286 (Farö Deep, lower plots): left plots with profiles of N_2O, N_2O equilibrium concentration, NO_3^-, NO_2^-; right plots with profiles of temperature, salinity and oxygen, the arrows indicate local N_2O minima, abbreviations see Fig. 2; **(b)** ΔN_2O plotted against oxygen (at all stations in the Eastern Gotland Basin, $y=-0.019\ x+5.625$, $R^2=0.67$ (except for $O_2<3\,\mu mol\,L^{-1}$)); **(c)** ΔN_2O plotted against NO_3^- (at all stations in the Eastern Gotland Basin, $y=0.639\ x-0.459$, $R^2=0.62$ (except for $O_2<3\,\mu mol\,L^{-1}$)).

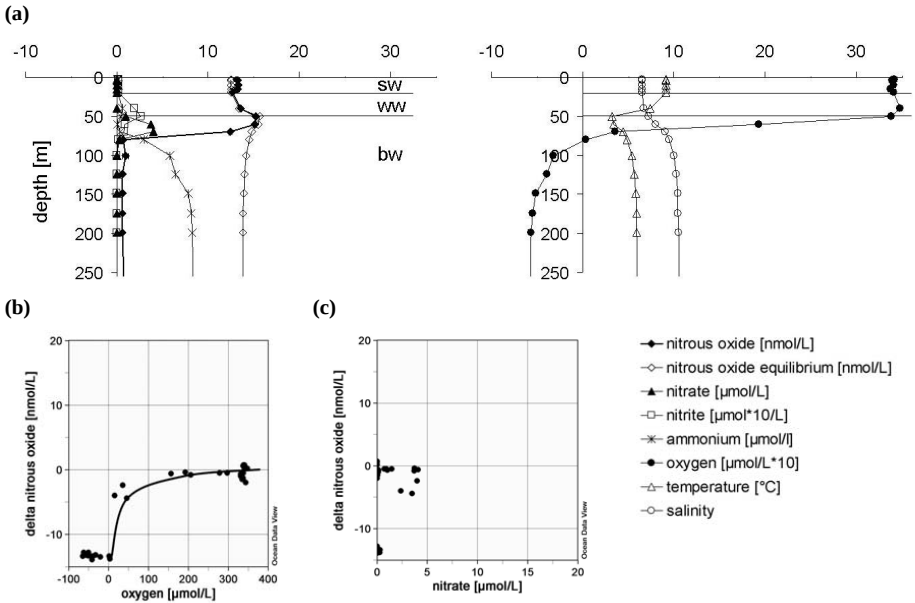

Fig. 7. Western Gotland Basin; **(a)** station 284 (Landsort Deep): left plot with profiles of N_2O, N_2O equilibrium concentration, NO_3^-, NO_2^-, right plot with profiles of temperature, salinity and oxygen, abbreviations see Fig. 2; **(b)** ΔN_2O plotted against oxygen (at all stations in the Western Gotland Basin; y=2.2467 Ln (x)−13.322, R^2=0.86, (with exception of O_2<0 μmol L^{-1})); **(c)** ΔN_2O plotted against NO_3^- (at all stations in the Western Gotland Basin).

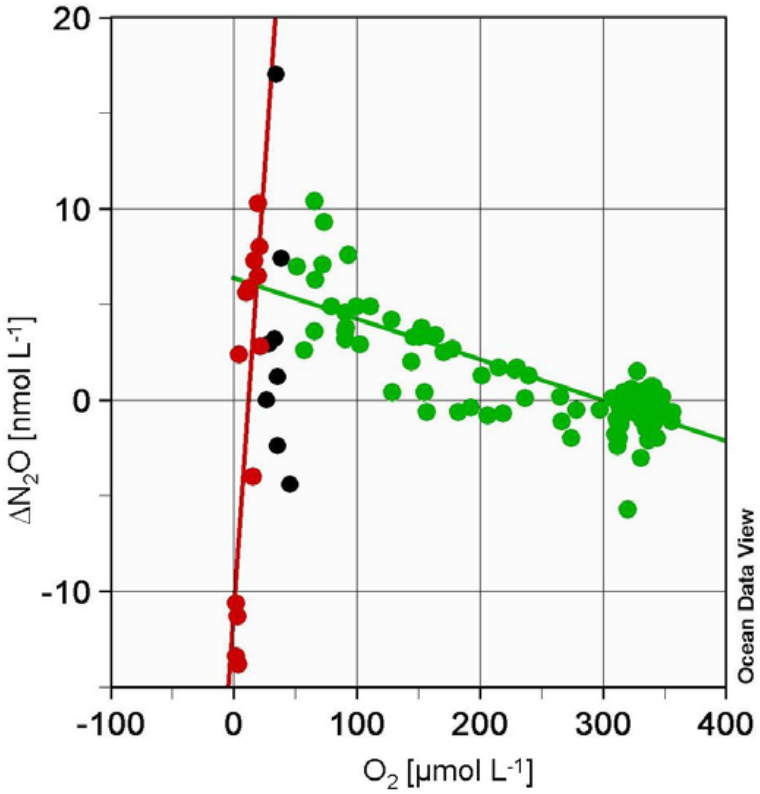

Fig. 8. Correlation between ΔN_2O and O_2 in the Baltic Sea. Correlations were calculated for oxic waters with O_2 concentrations >50 μmol L^{-1} (green coloured, y=−0.019 x+5.41, R^2=−0.70) and <20 μmol L^{-1} (red coloured, y=1.038 x−11.36, R^2=0.81). These concentrations were empirically tested and gave the best fittings for both correlations.

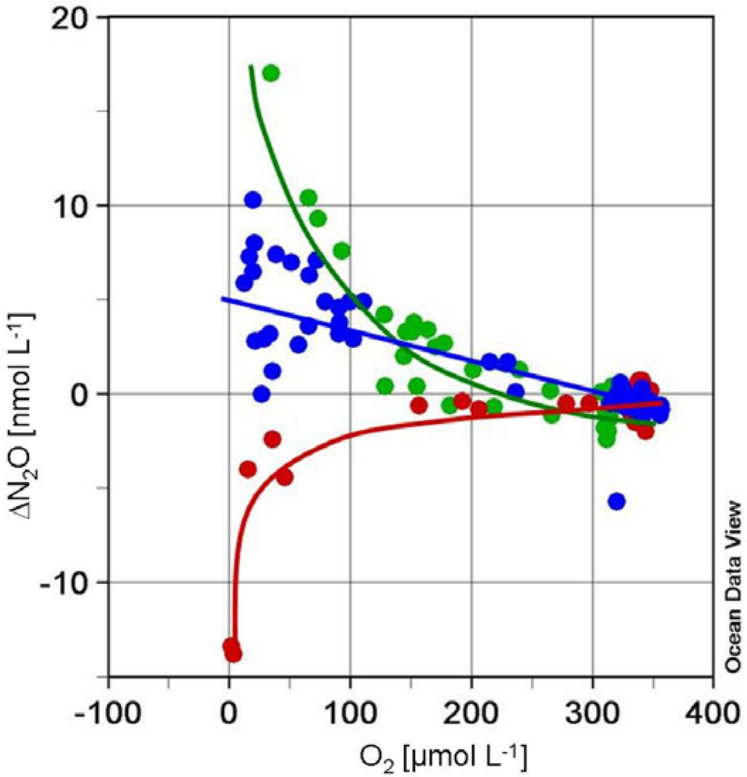

Fig. 9. Correlation between ΔN_2O and O_2 in the Baltic Sea; Correlations were calculated for the Bornholm Basin (station 140, 200, 213, 222, green coloured, $y=-6.83\,Ln(x)+37.88$, $R^2=0.86$), the eastern Gotland Basin (station 259, 250, 260, 271, blue coloured, $y=-0.02\,x+5.88$, $R^2=0.70$) and the western Gotland Basin (station 284, 240, 245, red coloured, $y=2.25\,Ln(x)-13.32$, $R^2=0.86$). Anoxic data and station 286 were excluded.